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PHOSPHACYCLOBUTANE AS A POSSIBLE INTERMEDIATE IN THE REACTION OF CARBETHOXYMETHYLENETRIPHENYLPHOSPHORANE WITH ACRYLONITRILE

J. D. McClure

Shell Development Company
Emeryville, California 94608

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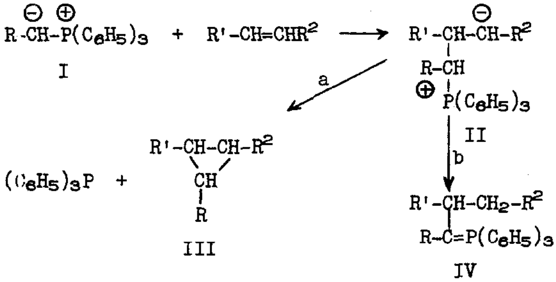
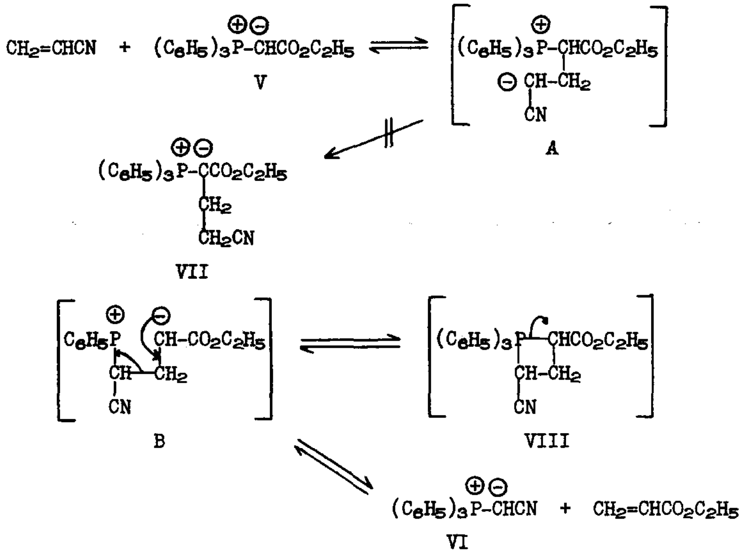
Bestmann and co-workers have systematically investigated the reactions of alkylidenephosphoranes with compounds containing an activated C-C double bond (1). It was found that the betaine (II) initially formed by addition to the double bond reacted subsequently by one of two reaction paths (a or b) and that the path actually taken depended upon the nature of the substituent R in the alkylidenephosphorane (I). If R was electron-releasing (path a), the betaine (II) eliminated triphenylphosphine (2,3) and formed a cyclopropane derivative (III). When R was electron-withdrawing (path b), the hydrogen on the carbon alpha to the triphenylphosphino group migrated to the negative center of the molecule (3) with formation of a Michael adduct (IV).



We have examined the reaction of a phosphorane containing an electron-withdrawing substituent with a compound containing an activated C-C double bond and report here that the reaction takes a different course from either of those described by Bestmann.

Reaction of carbethoxymethylenetriphenylphosphorane (V) with an equimolar amount of acrylonitrile in benzene solution at 90°C affords a crystalline product, $C_{20}H_{16}NP$ (VI), in 90% yield at 68% conversion of either nitrile or phosphorane. The product has been identified as the ylid, cyanomethylenetriphenylphosphorane, by comparison of its melting point with that of authentic sample prepared by dehydrohalogenation (4) of cyanomethyltriphenylphosphonium chloride. Ethyl acrylate is also obtained in 75% yield and has been characterized by a comparison of its spectral properties with those of an authentic sample. No product with structure VII could be isolated.



In effect, a "transylidation" reaction has occurred with the rupture of a C-C single bond. To our knowledge, this is the first example of a transylidation in which the transfer of hydrogen halide from one ylid to another has not been involved (5). A possible mechanism for the formation of VI and acrylate involving a phosphacyclobutane intermediate[a][b] (VIII) is shown above. Two analogies for such a transformation involving acetylenes instead of ethylenic compounds have recently appeared in the literature. Thus, certain phosphoranes (6,7) react with dimethyl acetylenedicarboxylate to give phosphorane adducts (IX) whose formation can best be rationalized by postulating a four-membered phosphorus-containing ring intermediate (X).

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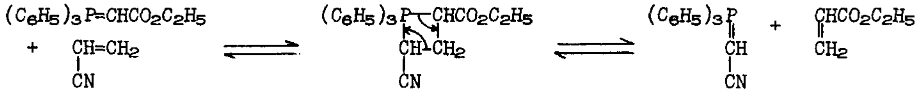
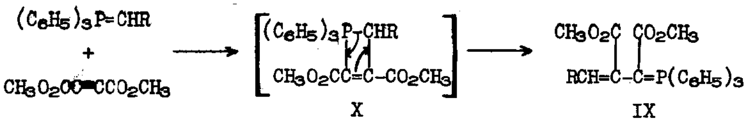
a) An alternative mechanism for transformation of A to B involving VIII as a "transition state" rather than as an intermediate is also equally valid.

b) A concerted four-centered cycloaddition mechanism may also be drawn but appears unlikely in view of recent theoretical arguments (8) bearing on similar transformations.





Certain phosphinimes (9) have also been found to undergo a similar type of reaction when treated with dimethyl acetylenedicarboxylate. The reaction discussed in this report differs from both of the reactions described in the literature in that the hypothesized intermediate is a phosphacyclobutane rather than a phosphacyclobutene. Although ring closure might be expected to be more facile for the formation of VIII, the ring opening step would be more difficult with VIII than with X since the driving force accompanying the formation of a totally conjugated product (IX) is not present in the transformation VIII ⇌ B.

EXPERIMENTAL

A solution of 63.0 g (0.18 mole) of V and 9.6 g (0.18 mole) of acrylonitrile in 350 ml of benzene in a 1-liter glass-lined stirred autoclave sealed under nitrogen was maintained at 90° for 16 hours. Solvent and volatile products were removed by distillation under reduced pressure. Analysis by gas-liquid chromatography at 80°C on a 20-foot column packed with DC-710 on fluoropak showed that the distillate contained 3.3 g (65% conversion) of acrylonitrile and 9.0 g (75% yield) of ethyl acrylate. Separation of the ethyl acrylate from the other components was effected by preparation gas-liquid chromatography. The IR and NMR spectra of the ethyl acrylate thus collected were identical with those of an authentic sample.

The residual solid was crystallized from 400 ml of benzene to give 33.5 g (90% yield) of white crystals, m.p. 135-190°C. After an additional recrystallization, VI melted at 192-193°. (Found: C, 79.6; H, 5.40; N, 4.45; P, 10.0. Calc. for $C_{20}H_{16}NP$: C, 79.7; H, 5.33; N, 4.65; P, 10.3.) No depression in melting point was observed when admixed with an authentic sample (4). Recrystallization from ethyl acetate of the solid remaining after removal of the benzene afforded 20 g (68% conversion) of carbethoxymethylenetriphenylphosphorane, m.p. 121-122°.

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